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Dielectric Behavior of Ethylenediamine Oligomer

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Dielectric properties of the ethylenediamine oligomer, $\text{H}_2\text{NC}_2\text{H}_4(\text{HNC}_2\text{H}_4)_{n-1}\text{NH}_2$ ($n=1, 2, 3$, and 4) were studied in order to elucidate the molecular behavior in liquid and supercooled states.

Dielectric measurements have been made at frequencies from 7.5 Hz to 5 MHz over the temperature ranges of -78.5 to $+60^\circ\text{C}$ in ethylenediamine and triethylenetetramine, and of -100 to $+60^\circ\text{C}$ in diethylenetriamine, respectively. Some related physical constants of these compounds were determined. It has been found that in these oligomers the static dielectric constants were related to the dipole moments by the Onsager equation and that the temperature dependence of the dielectric constants was well represented empirically by the equation

$$\epsilon = a + b/T,$$

where a and b are empirical constants and T the absolute temperature.

In supercooled state the oligomers exhibited a dielectric relaxation which was interpreted as superposition of the circular arc and the skewed arc relaxations.

INTRODUCTION

It is well known that some hydrogen-bonded liquids such as water and n -alcohol show a large primary dielectric relaxation which is expressed by Debye's equation or a semi-circle¹⁾ and that the strong intermolecular hydrogen bonding between the end OH groups plays an important role in the relaxation. In the ethylene glycol oligomer²⁾ the dielectric behavior also exhibited the evidence of strong hydrogen bonding between OH groups and showed some distribution of relaxation times which was due to the local orientation of part of the molecule in addition to the orientation of the molecules as a whole.

Although the NH_2 groups are capable of hydrogen bonding formation, the dielectric behavior of compounds having the NH_2 and NH groups are not extensively studied yet. In the present work dielectric studies of the ethylenediamine oligomer, $\text{H}_2\text{NC}_2\text{H}_4(\text{HNC}_2\text{H}_4)_{n-1}\text{NH}_2$ ($n=1, 2, 3$, and 4), were undertaken in connection with the contribution of hydrogen bond to the dielectric behavior of this oligomer. Also an interest was taken in dielectric relaxation of these non-rigid molecules.

This paper reports the static dielectric constant and their relation to the intermolecular hydrogen bonding and also dielectric relaxations in the supercooled liquid state.

EXPERIMENTAL

Materials

The oligomer samples used are ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA) which

* 篠 英之

were prepared by fractional distillation of commercial products from Union Carbide Corporation. Commercial ethylenediamine was dried over sodium and fractionally distilled three times at a reduced pressure of nitrogen; b.p. 32° (22 mm); m.p. 10.65°. Other commercial oligomers were purified by drying over Drierite and by successive fractional distillations under reduced nitrogen atmosphere. Diethylenetriamine: b.p. 65° (1.7 mm); m.p. -39.7°. Triethyleneteramine: b.p. 111° (1.4 mm). Tetraethylenepentamine: b.p. 152° (1.7 mm). Purified samples were kept under dry nitrogen atmosphere.

Measurements

A Type TR-1-A Transformer Bridge from Ando Electric Company was employed for measurements of capacitance and conductance which worked over a frequency range from 7.5 Hz to 5 MHz. The dielectric cell consisted of concentric platinum cylinders; the cell constant was determined by use of standard liquids. For dielectric measurements below dry ice temperature the temperature control bath was filled with a non-flammable mixture³⁾ and cooled by liquid nitrogen. An Au-Co versus Cu thermocouple was convenient for measurements of low temperature.

Density measurements were made with a pycnometer of the Lipkin type and refractive indices were measured by a Pulfrich refractometer. Refractive indices and densities of the oligomers are tabulated together with literature values in Tables 1 and 2, respectively.

The samples were transferred into the cell and the pycnometer in a dry box filled with nitrogen to avoid the contamination by moisture and carbon dioxide

Table 1. Refractive indices n_D of ethylenediamine oligomers.

Temp., °C	EDA	lit. ⁴	DETA	TETA	TEPA
20	1.45677	1.45677	1.48443	1.49847	1.50595
25	1.45418	1.4513	1.48216	1.49640	1.50400
30	1.45169		1.47980	1.49224	1.50188
40	1.44681		1.47523	1.49018	1.49788

Table 2. Densities of ethylenediamine oligomers in g/ml.

Temp., °C	EDA		DETA		TETA		TEPA	
		lit. ⁴		lit. ⁵		lit. ⁵		lit. ⁵
20	0.8978	0.8977	0.9517	0.9525	0.9791	0.9794	0.9939	0.9962
25	0.8934		0.9478		0.9751		0.9903	
30	0.8885		0.9436		0.9711		0.9864	
40	0.8792		0.9352		0.9632		0.9787	
50	0.8697		0.9267		0.9553		0.9715	

in air.

RESULTS AND DISCUSSION

Static Dielectric Constant

Static dielectric constants of EDA, DETA, TETA, and TEPA are listed in Table 3. These ethylenediamine oligomers showed relatively small dielectric constants in comparison with strongly hydrogen-bonded liquids such as *n*-alcohols and

Table 3. Static dielectric constants of ethylenediamine oligomers.

Temp., °C	EDA lit. ⁶ (100kHz)	DETA	TETA	TEPA
-60	...	20.09	16.97	14.39
-50	...	18.86	15.93	13.60
-40	...	17.88	14.97	12.90
-30	...	16.87	14.13	12.21
-20	...	15.87	15.35	11.57
-10	...	14.97	12.56	10.93
0	15.32	14.11	11.85	10.37
10	14.56	15.2 (9.70°C)	11.35	9.92
20	13.82	14.5 (17.40°C)	10.76	9.40
30	13.18	13.5 (26.50°C)	10.21	9.00
40	12.54	11.41	9.72	8.57
50	12.01	10.82	9.27	8.22
60	11.33	10.26	8.87	7.90

polyethylene glycols. The larger the molecule in this homolog, the smaller was the dielectric constants, because of a decrease in concentration of the end NH₂ group with increasing the molecular dimension. DETA, TETA, and TEPA are easily supercooled down to about -80°C. No discontinuity was observed in the curve of dielectric constant *versus* temperature between liquid and supercooled liquid states as shown in Fig. 1. This indicates that these three compounds have the freedom of dipole orientation in the supercooled state. The dielectric constant of EDA dropped abruptly at the melting point, showing a small value in the crystalline solid state.

Kimura, Toshiyasu, and Fujishiro⁷⁾ and Okamoto *et al.*⁸⁾ studied the dipole moment of this particular oligomer and found that the observed dipole moments in benzene solutions were in good agreement with those calculated under the assumption of free rotation around the C-C and C-N bonds. The Kirkwood equation correlates the static dielectric constant with the dipole moment⁹⁾

$$\epsilon_0 = \epsilon_\infty + \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \cdot \frac{4\pi N_0 g \mu_0}{3kT};$$

$$g = 1 + z \langle \cos \theta \rangle,$$

where ϵ_0 is the static dielectric constant, ϵ_∞ the dielectric constant at infinite frequency, μ_0 the molecular dipole moment in vacuum, N_0 the number of dipoles in cubic centimeter, g Kirkwood's correlation factor, Z the number of the nearest neighbor, $\langle \cos \theta \rangle$ the average of cosine of the angle between the reference dipole

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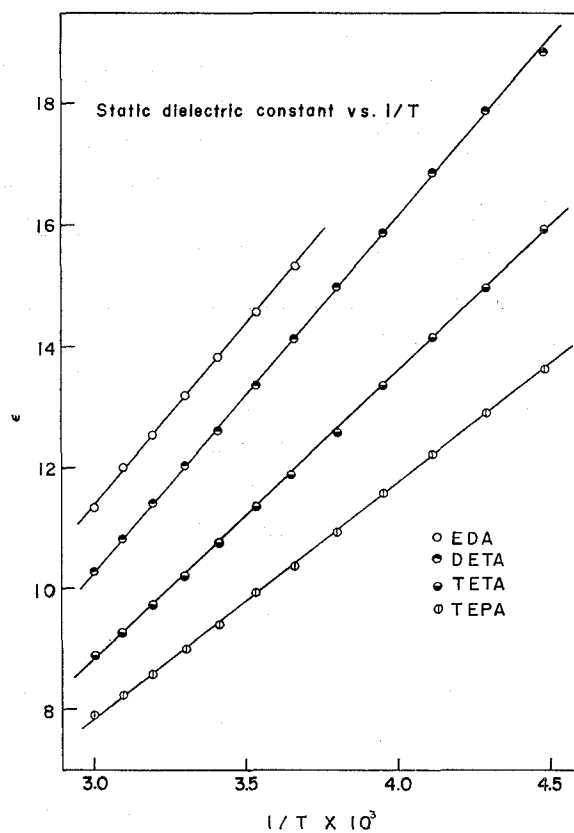


Fig. 1. Plots of static dielectric constants of ethylenediamine oligomers versus reciprocal of absolute temperature.

and its Z neighbors, and k and T have the usual significance.

The values of g for these compounds obtained from the dielectric constants

Table 4. Kirkwood g factors of ethylenediamine oilgomers.

Temp., °C	EDA	DETA	TETA	TEDA
-60	1.20
-50	...	1.34	...	1.20
-40	...	1.33	1.19	1.19
-30	...	1.32	1.18	1.18
-20	...	1.31	1.17	1.17
-10	...	1.29	1.15	1.15
0	1.23	1.27	1.13	1.14
10	1.22	1.26	1.13	1.14
20	1.21	1.24	1.12	1.12
30	1.21	1.24	1.11	1.11
40	1.20	1.22	1.09	1.10
50	1.20	1.21	1.08	1.09
60	1.18	1.19	1.07	1.08

and the dipole moments⁹⁾ are nearly equal to 1 as shown in Table 4. This means that the short range interaction such as hydrogen bonding is rather weak in the ethylenediamine oligomer and that the N-H intermolecular hydrogen bond does not contribute much to the static dielectric constant. It was found that the ethylenediamine oligomer exhibits the behavior similar to non-hydrogen bonded polar liquid, as far as the static dielectric constant is concerned. Trouton's constant also indicates that the intermolecular interaction in this oligomer is weak, compared with the ethylene glycol oligomer, as shown in Table 5.

Table 5. Comparison of Trouton's constants of ethylenediamine¹⁰ and ethylene glycol¹¹ oligomers.

EDA	25.73	Ethylene	28.98
DETA	25.36	Diethylene	24.14
TETA	24.40	Triethylene	30.95
TEPA	23.88	Tetraethylene	36.66

These static dielectric constants in liquid and supercooled liquid states increase linearly with the reciprocal of absolute temperature, as is the case with some other liquids, (Fig. 1) and can be expressed by the empirical relation

$$\epsilon_0 = a + \frac{b}{T},$$

where a and b are empirical constants. Numerical values of a and b are shown in Table 6.

Table 6. The numerical values a and b for the equation $\epsilon = a + b/T$.

	a	b
EDA	-6.547	5.9753×10^3
DETA	-7.364	5.8737×10^3
TETA	-5.460	4.7533×10^3
TEPA	-3.825	3.8893×10^3

Dielectric relaxation

Of these four compounds studied, only EDA crystallized easily at the melting point and the dielectric constant dropped to a small value. Solid EDA showed the wedge-type dispersion¹²⁾ which is often observed for ionic crystals, hydrogen-bonded organic solids and some solid systems with ionic impurity. Figure 2 shows the frequency dependence of the dielectric constant in the crystalline solid of EDA. The dispersion in this case may be caused by the ionic space charge due to the weak hydrogen bonding in the solid. With decreasing temperature, the intensity of this polarization decreased. This would be due to the decreased mobility of charge carrier. Other three compounds remained in the supercooled liquid state

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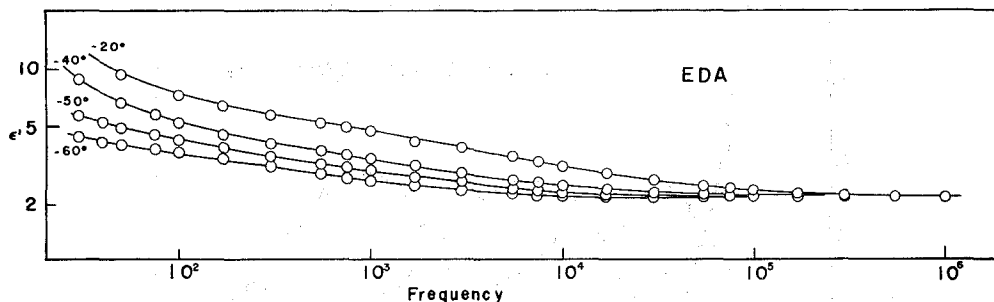


Fig. 2. Plots of $\log \epsilon'$ in the wedge type dispersion of EDA against frequency.

even at dry ice temperature and exhibited dielectric relaxation. The dielectric dispersion and absorption in DETA at various temperature are shown in Figs. 3 and 4, respectively. Figures 5 and 6 illustrate the frequency dependence of the dielectric constant and loss in TETA, respectively. As seen from Figs. 4 and 6, the curves of the dielectric loss *versus* logarithm of frequency are not symmetrical in these compounds.

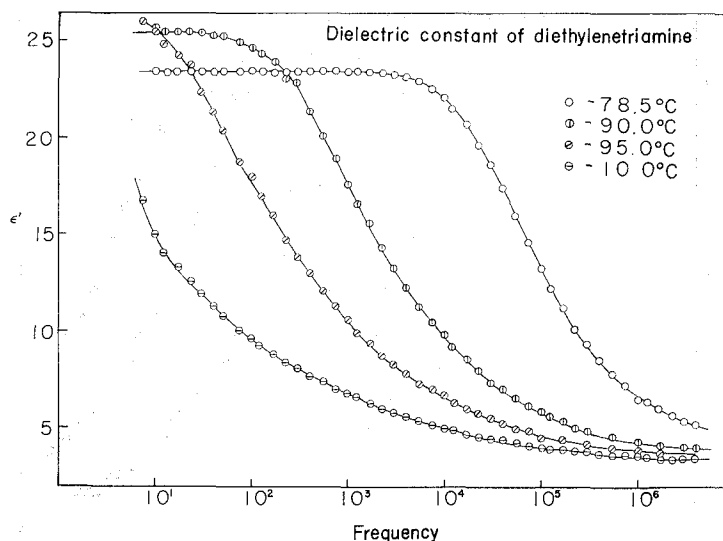


Fig. 3. Frequency dependence of dielectric constant of DETA.

In many cases the dielectric relaxation can be fitted by one of the following equations:

$$\begin{aligned} \epsilon^* &= \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} && \text{Debye type; }^{13)} \\ &= \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (j\omega\tau)^{1-a}} && \text{Cole-Cole or circular arc type; }^{14)} \\ &= \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + j\omega\tau)^\beta} && \text{Davidson-Cole or skewed arc type; }^{15)} \end{aligned}$$

where ϵ' is the real part of complex dielectric constant, ϵ'' the imaginary part of complex dielectric constant or the dielectric loss, ϵ_0 the static dielectric constant,

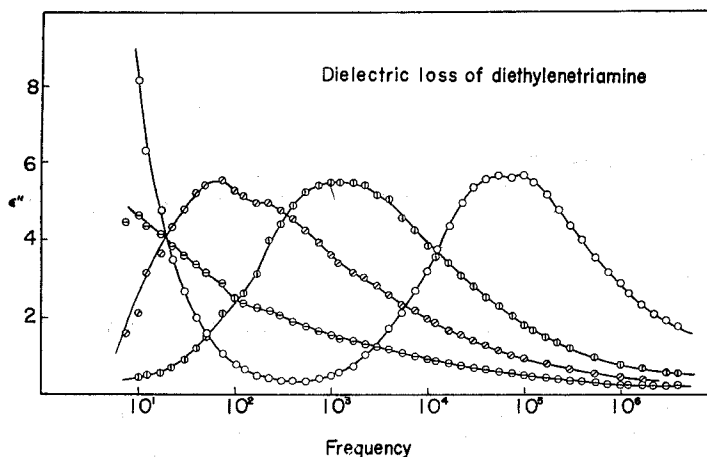


Fig. 4. Frequency dependence of dielectric loss of DETA.

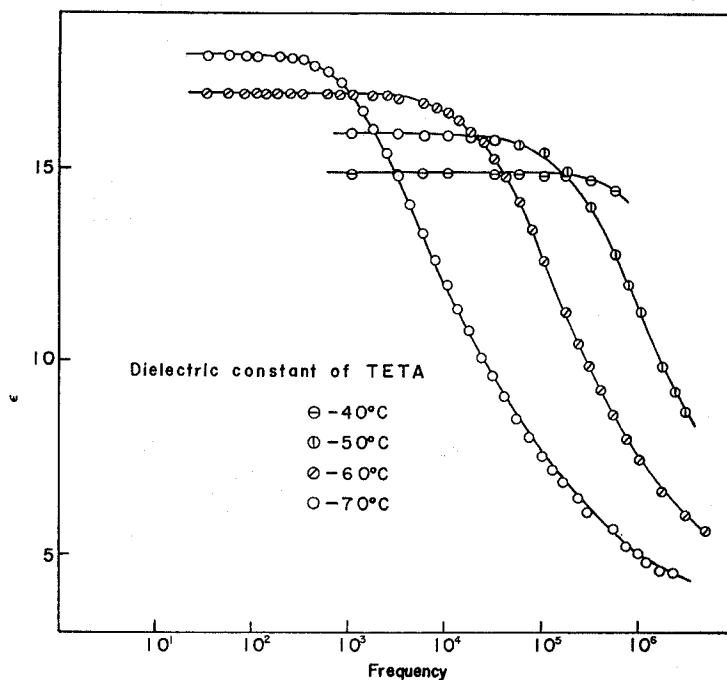


Fig. 5. Frequency dependence of dielectric constant of TETA.

ϵ_{∞} the limiting dielectric constant at high frequency, τ the mean relaxation time, ω the angular frequency, and α and β are parameters for the distribution of relaxation time.

With these polyethyleneimines except EDA the relaxation may be interpreted in terms of superposition of two types of relaxation. A typical example of overlapping of the absorption regions are shown for DETA in Fig. 7. The superposition of the relaxation regions is illustrated with DETA and TEPA in the complex plane plots in Fig. 8 and 9. With DETA and TETA the low-frequency relaxation was fitted by the Debye type and the high frequency one by the relaxation of

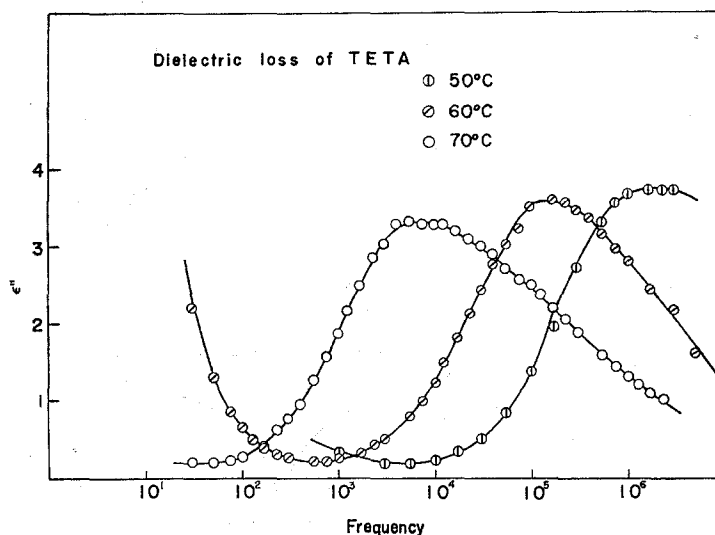
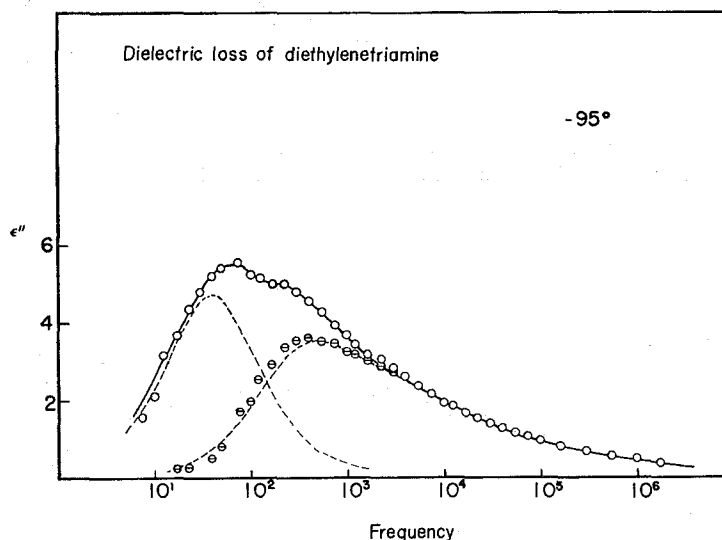


Fig. 6. Frequency dependence of dielectric loss of TETA.


 Fig. 7. Dielectric loss of DETA. Dashed curves represent calculated curves for the Debye type and the skewed arc relaxation of $\beta = 0.35$ and circles \ominus show the residual dielectric loss when the Debye type absorption is subtracted from the total loss.

the skewed arc type (Fig. 8). However in the case of TEPA the observed relaxation was separated into the circular arc and the skewed arc types as shown in Fig. 9. Therefore it was found that the dielectric relaxation in these oligomers was expressed

$$\epsilon^* = \epsilon_{\infty 2} + \frac{\epsilon_{01} - \epsilon_{\infty 1}}{1 + (j\omega\tau_1)^{1-\alpha}} + \frac{\epsilon_{02} - \epsilon_{\infty 2}}{(1 + j\omega\tau_2)^\beta}$$

where ϵ^* ($\epsilon = \epsilon' - j\epsilon''$) is the observed complex dielectric constant ; subscripts 1 and

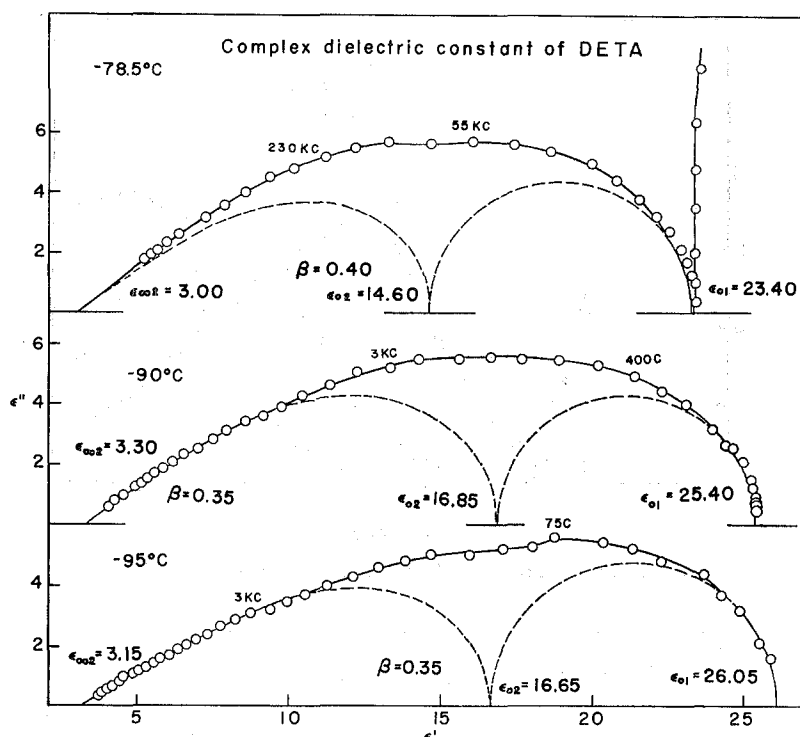


Fig. 8. Complex dielectric constants of TETA. Solid and dashed curves show observed and calculated curves, respectively.

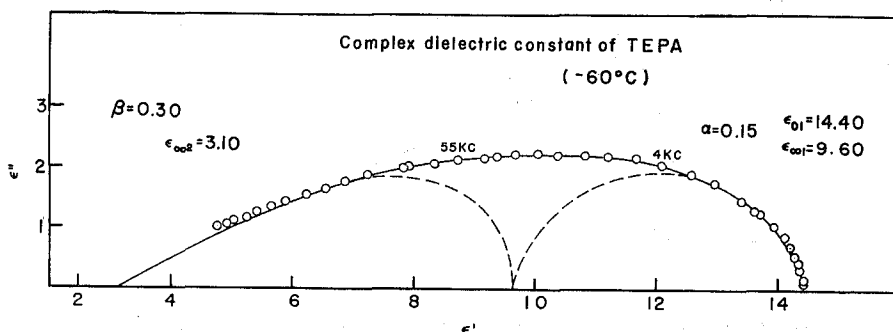


Fig. 9. Complex dielectric constants of TEPA.

2 mean the low- and high- frequency relaxation regions, $\epsilon_{\infty 1} = \epsilon_{02}$, $1 > \alpha \geq 0$ and $1 > \beta > 0$.

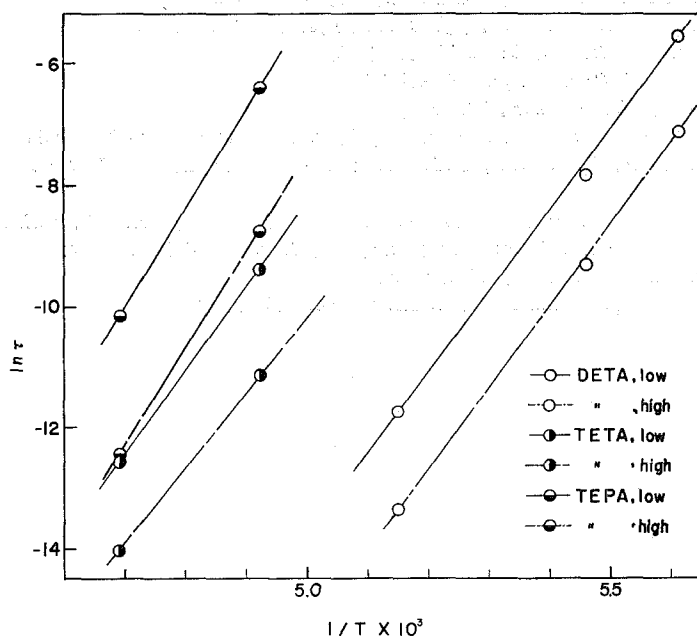
It has been reported that the supercooled state exhibits the skewed arc relaxation in some compounds such as glycols^{15,16,2)} and alkyl halides¹⁹⁾. Other types of dielectric relaxation^{18,19)} have been discussed concerning the distribution of relaxation times. The superposition of two different types of relaxation as is the case with the present work has been suggested for a few examples^{20,21)}.

Meinzel and Martin²²⁾ studied the dielectric relaxation of alkyl halides in the supercooled state and found that the dipole relaxation depended on the rate of

solidification and might be explained by conformational isomerism of non-rigid molecules. They also suggested that in general at least two dispersions might appear at the supercooled state for organic compounds and that the activation energy was greater than 1 eV and the entropy was about 100 eu²³⁾. The relaxation times in low- and high-frequency regions of DETA, TETA and TEPA are listed in Table 7. Logarithm of the relaxation times are plotted against reciprocal of the absolute temperature in Fig. 10. The activation enthalpy and entropy obtained for these oligomers are 25 kcal/mole and 100 eu in both low- and high-frequency relaxations. These results are very similar to those of 2-methyl pentanediol 2, 4²¹⁾.

Table 7. The relaxation times of ethylenediamine oligomers.

Temp., °C	DETA		TETA		TEPA	
	Low frequency	High frequency	Low frequency	High frequency	Low frequency	High frequency
-60	3.54×10^{-6}	7.96×10^{-7}	3.98×10^{-5}	3.98×10^{-6}
-70	8.61×10^{-5}	1.45×10^{-5}	1.68×10^{-3}	1.59×10^{-4}
-78.5	7.96×10^{-6}	1.59×10^{-6}
-90	3.98×10^{-4}	9.10×10^{-5}
-95	3.98×10^{-3}	7.96×10^{-4}

Fig. 10. Plots of logarithm of relaxation time *versus* reciprocal absolute temperature.

The molecular mechanism of these two relaxations have not been made clear. However it may be considered that the low-frequency relaxation is attributed to the dipole orientation of the molecule as a whole and that the high-frequency

relaxation from the segmental motion of the molecule.

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